

論文 / 著書情報
Article / Book Information

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Title(English)	Study on Novel Preparation Process of Olivine Cathode Materials with High Working Potentials and Their Cathode Performance for Lithium Batteries
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種別(和文)	論文要旨
Type(English)	Summary

論文要旨

THESIS SUMMARY

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要旨（英文 800 語程度）

Thesis Summary (approx.800 English Words)

Lithium cobalt phosphate (LiCoPO_4) and Lithium nickel phosphate (LiNiPO_4) are expected to be the next generation cathode materials for lithium ion batteries, mainly because of their thermally stable structures, high working potentials and high theoretical capacity (167 mAh g^{-1}). Nevertheless, poor electronic and ionic conductivities of the LiCoPO_4 and LiNiPO_4 cathode materials hinder their applications. To overcome those problems, the LiCoPO_4 and LiNiPO_4 cathode materials were prepared by aerosol and powder technologies in this study. The objective of this study was to improve the electrochemical performance of LiCoPO_4 and LiNiPO_4 .

In the chapter 1, the background of energy crisis and the importance of development of renewable energy systems were demonstrated. The rechargeable batteries were introduced as energy storage systems, especially the lithium ion batteries. The cathode materials for lithium ion batteries, particularly LiCoPO_4 and LiNiPO_4 , were laid emphasis on, since they could exhibit very high energy densities. The most significant problems of the LiCoPO_4 and LiNiPO_4 cathode materials were revealed. Furthermore, the examples of the recent publications on the LiCoPO_4 and LiNiPO_4 cathode materials were introduced, and then the challenges of the reported synthesis approaches were pointed out in this chapter. Finally, the objective of this study was presented.

In the chapter 2, LiCoPO_4/C composites were prepared by a combination of spray pyrolysis and wet ball milling followed by further heat treatment. The effect of various synthesis parameters, such as annealing temperature, rotation speed, content of carbon and

various carbon sources on the physical and electrochemical properties of LiCoPO₄/C composites were studied. The effect of crystallinity, carbon content and impurity phase Co₂P on the electrochemical properties of LiCoPO₄/C composites was confirmed. The LiCoPO₄/C composites showed a high discharge capacity of 97 mAh g⁻¹ in a voltage range of 3.5-5.1 V at 0.1C rate and good cycle performance after 50 cycles, due to the reduced particle size and introduced conductive carbon. However, this discharge capacity was still low compared with the theoretical capacity, probably because of the large particle size (200 nm) of the LiCoPO₄/C composites.

In order to restrict the particle size of LiCoPO₄, the citric acid was added in the precursor solution as a dispersing agent in the chapter 3. Then, the spherical nanostructured LiCoPO₄ particles (SN-LiCoPO₄) were successfully synthesized by citric acid assisted spray pyrolysis in air atmosphere. The effect of the spray pyrolysis temperature and addition of the citric acid additive in the precursor solution on the physical and electrochemical properties of the LiCoPO₄ samples were investigated. The field-emission scanning electron microscopy images showed that with addition of citric acid in the precursor solution, the growth of primary particle sizes of synthesized SN-LiCoPO₄ could be restricted and the specific surface area of the SN-LiCoPO₄ increased significantly. When evaluated as cathode in lithium batteries in a voltage range of 2.0-5.1 V at 0.05C, the SN-LiCoPO₄ electrode showed a high discharge capacity of 135 mAh g⁻¹, which reached to 81% of the theoretical capacity. The electrochemical impedance spectroscopy (EIS) data demonstrated that the SN-LiCoPO₄ electrode had lower resistances and faster redox reaction kinetics compared with bare LiCoPO₄. The excellent electrochemical performance of SN-LiCoPO₄ electrode could be attributed to the diminished primary particle size that shortened the lithium ion diffusion pathway.

Due to the possibility that LiNiPO₄ can deliver higher working potential, in the chapter 4, LiNiPO₄/C composites were prepared by a combination of spray pyrolysis and wet ball milling followed by further heat treatment. The effect of spray pyrolysis temperature,

annealing temperature and rotation speed on the physical and electrochemical properties of synthesized LiNiPO_4/C composites were examined. LiNiPO_4/C composites showed a charge capacity of 73 mAh g^{-1} with a voltage plateau at 5.1 V and an extremely low discharge capacity of 8 mAh g^{-1} in a voltage range of $3.5\text{-}5.3 \text{ V}$ at 0.1C rate, which was due to the poor electronic conductivity of LiNiPO_4 .

To further improve the electrochemical properties of LiNiPO_4 , Co doping was considered in the chapter 5, since the electronic conductivity of LiCoPO_4 is higher than that of LiNiPO_4 . Then, $\text{LiNi}_{1-x}\text{Co}_x\text{PO}_4/\text{C}$ ($x=0, 0.2, 0.5, 0.8, 1$) nanocomposites were prepared by a combination of spray pyrolysis and wet ball milling followed by further heat treatment. The effect of cobalt doping content, wet ball milling and carbon introduction on the physical and electrochemical properties of synthesized $\text{LiNi}_{1-x}\text{Co}_x\text{PO}_4/\text{C}$ nanocomposites were studied. The formation of $\text{LiNi}_{1-x}\text{Co}_x\text{PO}_4$ solid solutions was confirmed from the linearly change of lattice parameter (a, b, c) with content of Co (x). The first discharge capacities of $\text{LiNi}_{1-x}\text{Co}_x\text{PO}_4/\text{C}$ nanocomposites were superior to those of bare $\text{LiNi}_{1-x}\text{Co}_x\text{PO}_4$ samples. In addition, the electrochemical activity of $\text{Ni}^{2+}/\text{Ni}^{3+}$ redox couple in the $\text{LiNi}_{0.5}\text{Co}_{0.5}\text{PO}_4/\text{C}$ electrode was firstly discovered from the reduction peak of the cyclic voltammetry curve at 4.7 V in the normal electrolyte system. The EIS data demonstrated that the $\text{LiNi}_{0.5}\text{Co}_{0.5}\text{PO}_4/\text{C}$ electrode had low resistances and fast redox reaction kinetics. The excellent electrochemical properties of $\text{LiNi}_{0.5}\text{Co}_{0.5}\text{PO}_4/\text{C}$ were due to the reduced particle sizes and introduced conductive carbon.

備考：論文要旨は、和文 2000 字と英文 300 語を 1 部ずつ提出するか、もしくは英文 800 語を 1 部提出してください。

Note：Thesis Summary should be submitted in either a copy of 2000 Japanese Characters and 300 Words (English) or 1 copy of 800 Words (English).

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